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REVIEW AND UPDATE ON ELECTROCOMPOSITES

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FEBRUARY 1992

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92-08015

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REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington DC 20503

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE February 1992	3. REPORT TYPE AND DATES COVERED Final	

4. TITLE AND SUBTITLE

REVIEW AND UPDATE ON ELECTROCOMPOSITES

5. FUNDING NUMBERS

MM&T Proj. 6706797
PRON: M1-0-23022

6. AUTHOR(S)

V.P. Greco

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army ARDEC
Benet Laboratories, SMCAR-CCB-TL
Watervliet, NY 12189-4050

8. PERFORMING ORGANIZATION REPORT NUMBER

ARCCB-TR-92005

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army ARDEC
Close Combat Armaments Center
Picatinny Arsenal, NJ 07806-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The demand for metal matrix composites (MMC) is reaching a new height in the material community in view of their superior strength at elevated temperatures. Several methods are employed in producing these composites in which high strength inert particles, fibers, or filaments are incorporated in the matrix of a conventional metal. A critical problem in producing metal matrix composites is the handling and damaging of candidate brittle high strength fibers due to high process temperatures and pressures. A process for producing composites, which does not require high temperatures or pressures, is electrodeposition in aqueous solutions which offers a number of other benefits. Electrocomposites are reinforced electrodeposits or electroforms with high strength inert particles, fibers, or continuous filaments. From a review of the literature, an updated evaluation of electrocomposites is given, followed by a review of their strengthening mechanisms and the proposed theories of particle encapsulation. The results and properties of electrocomposites previously reported are also reviewed and the future role that platers have in producing high performance composites, which outperform superalloys, is assessed.

14. SUBJECT TERMS

Electrocomposites, Composites, Metal Matrix, Strengthening, Encapsulation, Mechanical Properties

15. NUMBER OF PAGES

44

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL

TABLE OF CONTENTS

TABLES

LIST OF ILLUSTRATIONS

INTRODUCTION

Composites are often described as polymers or resins which have been reinforced with glass filaments. In reality, any combination of two or more materials with each making a property contribution can be identified as a composite. Some composites are found in nature, such as bamboo and asbestos, and manmade composites date back to the caveman who reinforced mud bricks with straw. The most recent concepts which have been ushered into the arena of high performance materials are metal matrix composites which have high modulus and high strength retention at elevated temperatures.

The types* of metal matrix composites which are being considered in today's material community for high performance application are:

- dispersion-strengthened composites

- particle-reinforced composites

- composites reinforced with fibers, whiskers, or filaments

Fine inert particles or filamentary reinforcements with high temperature strengths combined with soft conventional matrix metals can produce composites which outperform superalloys.

The use of inert particles to improve mechanical properties of metals at elevated temperatures was first exploited in 1910 by Coolidge (ref 1) in thoriated tungsten to increase creep resistance. The first dispersion-strengthened material designed as a structural load-bearing system was sintered aluminum particles (SAP) in aluminum reported in 1952 (ref 2). Another dispersion-strengthened material that received considerable attention in the

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*Laminates are also an important type of composite, however, their laminae actually consist of the composites listed above, which means a series of thin composites bonded together producing a large composite. Therefore, these will not be discussed here.

1

early 1960s was thoria in nickel (ref 3), which is more commonly known as TD-nickel.

Whiskers (a major candidate reinforcement) were observed on silver ores as far back as the 19th century and were referred to as hair silver (ref 4). No attention was given to their growth, which was influenced by temperature and humidity, until they became a problem on tin plated electronic components causing an electrical short during World War II. These whiskers, which were observed as being strong and flexible, were identified as a plating reject and it wasn't until the early 1950's that they were intentionally grown in the laboratory (ref 5). The testing of tin whiskers (single crystals) was found to have strengths several hundred times that of bulk tin (ref 6). The latter results stimulated much interest, and studies on whisker growth of high modulus-high temperature refractory metals quickly followed.

The achievements in producing high strength whiskers followed by the remarkable development of high modulus-low density boron filaments in 1958 by Talley (ref 7) triggered the composite technology explosion. With the advanced developments that followed, some of the potential whiskers and filaments such as alumina, silicon carbide, boron, and graphite became commercially available on a very limited scale in the late 1960s.

It was during the latter decade that the concept of high performance man-made fiber-reinforced composites became a reality. The strength of conventional engineering materials is only a fraction of their theoretical strength and their usage in high temperature environments is very limited. However, we now have high temperature and low density fibrous or filamentary materials which do approach their theoretical strengths. Yet, these high modulus fibers or filaments, which have anisotropic properties, are unsuitable as a structural material in their monolithic state not only because of their very small

2

diameters, but due to their brittleness, their difficulty to handle in filamentary form, and their tendency to degrade in some atmospheres.

Therefore, by encapsulating these fragile high strength fibers or filaments in a suitable protective matrix metal, we can tailor the composite to our specific needs. Two important requirements in the search for these new materials are a high strength or high modulus/density ratio[†] and high thermal stability. The strength/density ratios of some of the candidate filamentary materials can be compared to some of the conventional engineering materials by reviewing Table I.

TABLE I. PHYSICAL AND MECHANICAL PROPERTIES OF SOME COMMON FILAMENT AND WHISKER MATERIALS*

Material	Melting Point (°C)	Modulus of Elasticity		Ultimate Tensile Strength		Density		Max. Modulus to Density Ratio
		x 10³ MPa	x 10⁶ psi	MPa	Ksi	g/cm³	lb/in.³	(x 10⁶ in.)
Copper	1083	100-117	14.5-17	338-552	49-80	8.97	.324	52
Tungsten	3460	400	58	3448-4275	500-620	19.24	.695	83
Titanium	1670	115	16.7	1931	280	4.91	.282	98
Steel	1605	200	29	3103-4137	450-600	7.81	.170	103
Aluminum	660	73.1	10.6	414-621	60-90	2.69	.097	109
E Glass	1315	73	10.5	2413-3448	350-500	2.55	.092	114
S Glass	1650	85.5	12.4	4317-4827	600-700	2.49	.090	138
Bamboo	.	33.4	4.8	345	50	0.50	.018	272
Asbestos	1520	172	25	1379	200	2.49	.090	278
SiC	2100	483	70	2068-2758	300-400	3.46	.125	560
Boron	2040	379-414	55-60	2068-3448	300-500	2.55	.930	278
Beryllium	1285	303	44	1310	190	1.85	.067	657
Graphite	3690	152-600	22-87	2758-3898	400-565	1.50	.054	1000
Alumina Whiskers	2080	414-1034	60-150	1379-24133	200-3500	3.96	.143	1049
SiC Whiskers	2705	483-1034	70-150	13790-41370	2000-6000	3.18	.115	1304
Graphite Whiskers	3650	1000	145	20685-24133	3000-3500	2.10	.076	1906

*Averages of various published values

In spite of these accomplishments in the development of reinforcements in the 1960s, interest in the implementation of MMC floundered in the early years mainly due to the unavailability and high cost of the reinforcements and fabrication of components. In more recent years, the cost of reinforcements has

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[†]It was often quoted in the early years that a bonus of $250 would be paid by the military for every pound that was saved in aerospace structural components.

3

decreased, but it is still considered high. However, they are more readily available on a commercial scale and their strengths and reproducibility have significantly improved. Also, due to the technological advancements in aerospace structures and high performance engines where conventional materials will not meet the new requirements, the demand for MMC is reaching a new height. These new composites may be regarded as one of the most potential classes of high strength structural materials of all times because of their versatility to be tailored to meet the requirements for severe high temperature environments.

However, some serious obstacles still have to be surmounted. Reproducibility, post-machining, welding, and quality acceptance testing are problem areas which are currently being explored. Because of the anisotropic properties of composites, the measurements of their properties, such as fatigue, fracture toughness, and thermal stability, are much more difficult to perform. Performance testing and property measurements are being given full attention by ASTM groups based on the series of meetings and symposiums focusing on composites on an international level. In 1980 the Department of Defense established a Metal Matrix Composite Information Analysis Center (MMCIAC) to promote the advancement of composite materials.

FABRICATION PROCESSES

Composites are being produced by several processes such as castings, powder metallurgy, extrusion, diffusion bonding, vacuum infiltration, etc. A common problem with the fabrication of composites is the handling and damaging of the fragile and reactive candidate filamentary reinforcements due to the high process temperatures and pressures. A process which does not require high temperatures and pressures is electrodeposition in an aqueous electrolyte which offers a number of other benefits.

4

In spite of the obvious advantages of producing composites by electrodeposition techniques, the plater does not appear to be keeping pace with the ambitious investigators who are exploiting other processes in their attempt to meet the demand for fiber-reinforced composite materials. In constrast to fiber reinforcements, electrocomposites containing particles are being produced by the plater, but the literature indicates that the bulk of the studies are being carried on in foreign countries. A review of the literature also implies that a closer interface is needed between the user and the fabricator of composite materials to produce high quality potential metal systems. In order to achieve this, the fabricator must have a clear understanding of the material-strengthening mechanisms and composite behavior, which is the intent of this report.

STRENGTHENING MECHANISMS

The dispersion-strengthening of metals or alloys by inert particles has been treated by a number of investigators (refs 8-12). The filament reinforcement of metals has been reported by Kelly and his co-workers (refs 12-15) among others (ref 16). The work by Grant (ref 10) and Kelly and Nicholson (ref 12) is most extensive; however, the proposed theories on strengthening are still incomplete. It should be sufficient for this discussion to briefly state the principal conclusions which have been established on the theory of strengthening. In addition, some of the simple equations are presented to predict the increase in composite strength without entering into the details of stress analysis or the associated dislocation mechanics. Some of these equations have previously been reported in the plating literature (refs 17,18), but will be repeated here in order to make this summary more comprenensive.

5

Characterization of the Three Composite Systems

• Dispersion-strengthened: This composite is characterized by a microstructure consisting of a metal matrix within which fine inert particles are uniformly dispersed. The particle diameter ranges from about 0.01 to 0.1 μm, and the volume percent (v/o) of the particles ranges from 1 to 15 percent.

• Particle-reinforced: This composite is characterized by dispersed inert particles of greater than 1.0 μm diameter with a v/o dispersoid usually in excess of 25 percent.

• Fiber-reinforced: This composite is characterized by the introduction of fibers or filaments aligned unidirectionally or randomly with dimensions and volumes ranging as follows:

Diameter: from submicron to several mils

Length: from mils to continuous lengths

Volume: from a few percent to more than 70 percent

Performance of the Different Composite Systems

Dispersion-strengthening:

The performance of a metal which has been strengthened by a dispersion of a low v/o of small fine encapsulated particles is as follows:

• The matrix metal carries the load.

• The hard, fine inert particles impede the motion of dislocations in the matrix; recrystallization and grain growth are retarded at high temperatures.

The first attempt to relate the particle dispersion with the shear strength of a matrix metal was proposed by Gensamer (ref 8) during his studies with steels in which he showed that the shear strength (ref 5) is directly proportional to the logarithm of the mean free path (λ) between carbide particles.

$$\sigma = -A\lambda + B \tag{1}$$

6

The theory receiving most attention was that of Orowan (ref 9) who considered only particle spacing:

$$\tau = Gb/D_p \tag{2}$$

where: τ = shear stress

    G = matrix shear modulus

    b = Burger's vector

    D_p = average spacing between particles

Gensamer (ref 8) showed that the mean free path λ and interparticle spacing D_p are related to the volume fraction V_p and mean particle diameter d through the relations:

$$\lambda = (2d/3V_p)(1-V_p) \tag{3}$$

and

$$D_p = (2d^2/3V_p)(1-V_p) \tag{4}$$

Typical ranges for these parameters in dispersion-strengthened composite materials are

$$\lambda - 0.3 \text{ to } 0.01 \ \mu m$$

$$D_p - 0.3 \text{ to } 0.01 \ \mu m$$

$$V_p - 0.01 \text{ to } 0.15$$

$$d - < 0.1 \ \mu m$$

Dispersion-strengthened alloys are mainly noted for their high creep resistance and retention of strength at elevated temperatures.

The behavior of two dispersion-hardened alloy systems as a function of temperature can be observed in Figure 1.

7
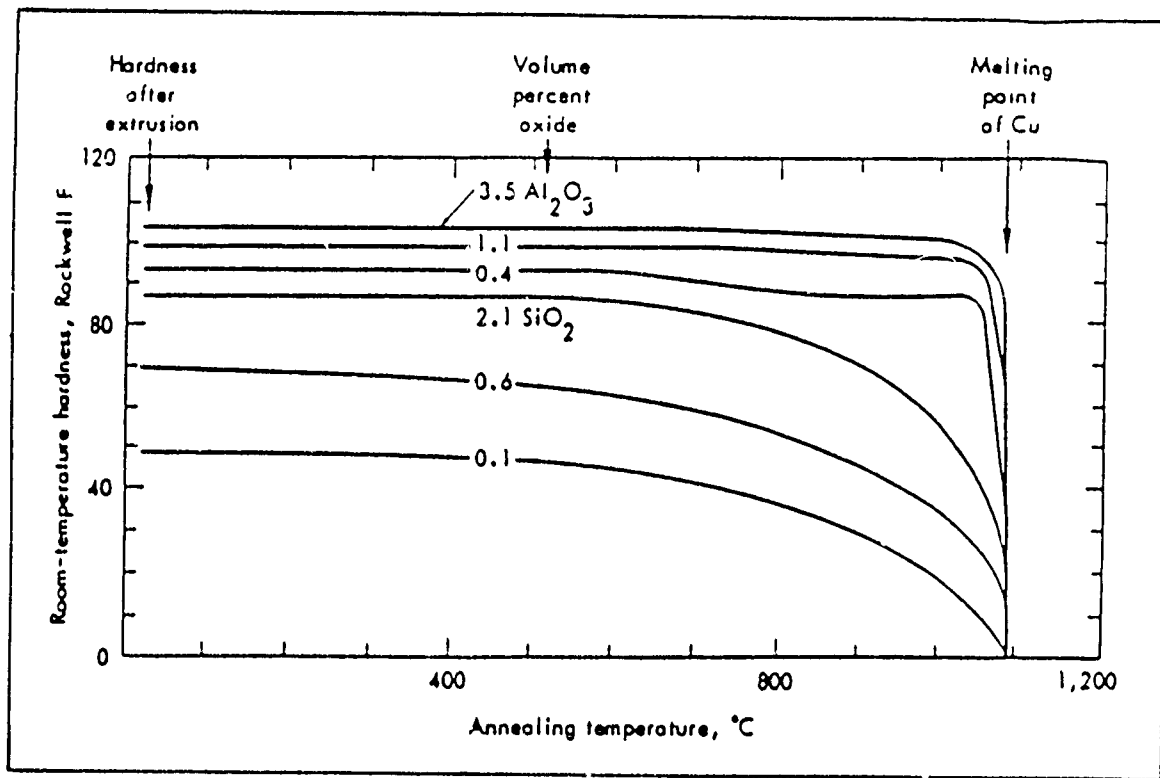
Figure 1. Hardness retention as a function of temperature for various copper-silica and copper-alumina dispersion-strengthened materials (ref 19).

Particle Reinforcement: (ref 20)

The performance of a metal which has been strengthened by a dispersion of high v/o of large coarse encapsulated particles is as follows:

• The matrix and dispersed particles share the load.

• Strengthening occurs initially when the dispersed particles restrict the matrix deformation by a mechanical constraint.

Since the elastic moduli of dispersed-particulate composites should follow an isostress modulus, any positive deviation from Eq. (5) which follows signifies matrix constraint. All systems investigated exhibit positive deivation and thus, matrix constraint.

$$E_c = \frac{E_m E_p}{V_m E_p + V_p E_m}$$ (5)

8

where: E = modulus of composite (c), matrix (m), or particle (p)

V = volume fraction of matrix (m) or particle (p)

- In a <u>ductile</u> metal matrix, the particle increases the local resistance of the matrix to slip and to undergo large plastic deformation.

- In a <u>brittle</u> matrix, the matrix is the primary load-carrying element and the ductile metal particles function by limiting the size of the largest or most severe flaw or crack that can occur in the brittle matrix.

Fiber or Filament Reinforcement:

The performance of a metal which has been strengthened by high strength-high modulus inert fibers or filaments is as follows:

- The fibers carry the load.

- Soft matrix protects fibers.

- Matrix transfers applied stress to high stress fibers.

Strength of Fiber Composites - Studies by McDanels et al. (ref 21)

have shown that the ultimate tensile strength of unidirectional continuous-fiber composites (σ_c) is expressed by the rule of mixtures:

$$\sigma_c = \sigma_m'V_m + \sigma_fV_f \qquad (6)$$

where: σ_m' = stress in matrix at the ultimate tensile strain of the fibers

V_m = volume fraction occupied by matrix

σ_f = ultimate tensile strength of fiber

V_f = volume fraction occupied by fiber

The equation assures a strong bond between the fiber and matrix metal without any interfacial reactions and neglects the interaction between the constituents due to the differences in their Poisson ratios. The insensitivity of the composite modulus, E_c, to the difference in constituent Poisson ratios has been treated in some detail by Tsai et al. (ref 22).

According to Kelly and Davies (ref 15), deformation of a composite with uniaxially aligned continuous fibers stressed parallel to the fibers proceeds in four stages as follows:

1. Both the fibers and the matrix deform elastically.

2. The fibers continue to deform elastically, but the matrix now deforms plastically.

3. Both the fibers and the matrix deform plastically (ductile fibers only).

4. The fibers fracture, followed by composite fracture.

In stage 1, the composite modulus, E, can be predicted by Eq. (6).

The linear relationship presented by Eq. (6) has been confirmed by several investigators (refs 23-26) reporting experimental data with the tungsten-copper and steel-silver systems.

Minimum and Critical Volume Fraction of Fibers - Equation (6) is valid only when the fibers exceed a certain minimum volume fraction in the composite (refs 15,27) as computed from the following relationship:

$$V_{min} = \frac{\sigma_m - \sigma_m'}{\sigma_f + \sigma_m - \sigma_m'} \qquad (7)$$

where σ_m = the ultimate tensile strength of the matrix.

The value of V_{min} increases as the strength of the fibers decreases or as the strength of the matrix approaches that of the fiber. In order for the composite strength to exceed the ultimate strength of the matrix, the volume fraction of the fibers must exceed a critical value, V_c, which is shown as follows:

$$V_c = \frac{\sigma_m - \sigma_m'}{\sigma_f - \sigma_m'} \qquad (8)$$

The critical volume increases as the degree of work-hardening in the matrix ($\sigma_m - \sigma_m'$) increases and also as the strength of the matrix approaches that of the fibers. The relative values of V_{min} and V_C are shown in Figure 2.
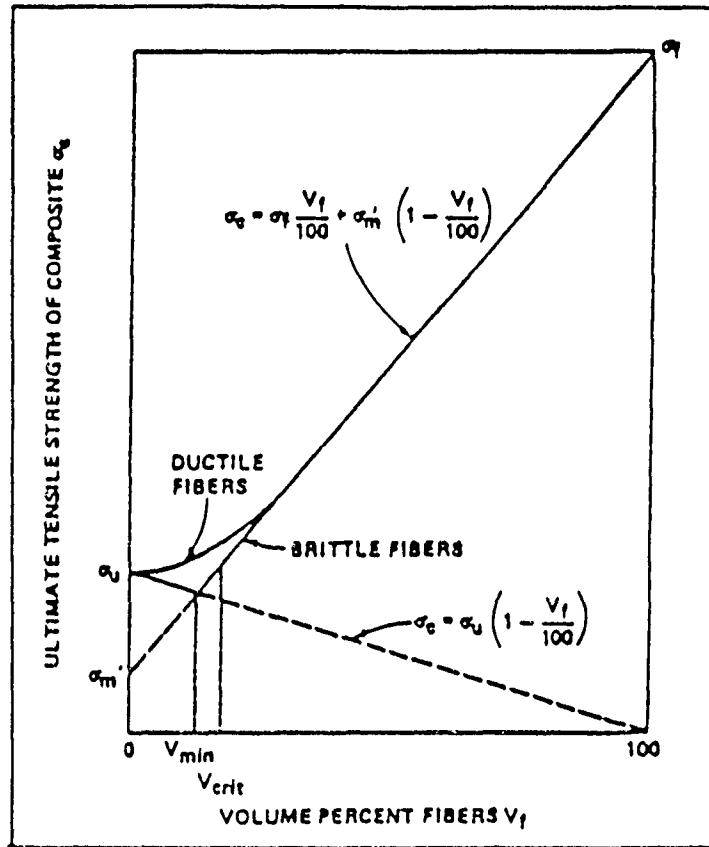
Figure 2. Theoretical values of composite strength σ_c with fiber content V_f for reinforcement with continuous fibers (ref 15).

Critical Fiber Length - When discontinuous fibers are used, the length of the fiber must be greater than a critical length, L_c, in order to achieve strengthening of the composite (refs 25-30). Figure 3 illustrates the stress distribution along a fiber length in relation to the critical length.

Different investigators (refs 14,24,31,32) have derived similar equations that relate discontinuous fiber-reinforced composite strength with the length of the fiber in the composite. Kelly and Tyson's equation (refs 14,24) is as follows:

$$\sigma_c = \sigma_m'(1 - V_f + \sigma_f(1 - \frac{l_c/D}{2l/D})V_f \ldots \tag{9}$$

11

where: ℓ/D = length-to-diameter ratio of fibers in composite

ℓ_c/D = critical length-to-diameter ratio of fiber necessary to stress

fiber to its ultimate tensile strength

The preceding equation is valid for values of ℓ/D equal to or greater than ℓ_c/D (critical aspect ratio). An approximate value for ℓ_c/D can be obtained from:

$$\ell_c/D = \sigma_f/2\tau \qquad (10)$$

where τ is the shear strength of the matrix or interface.
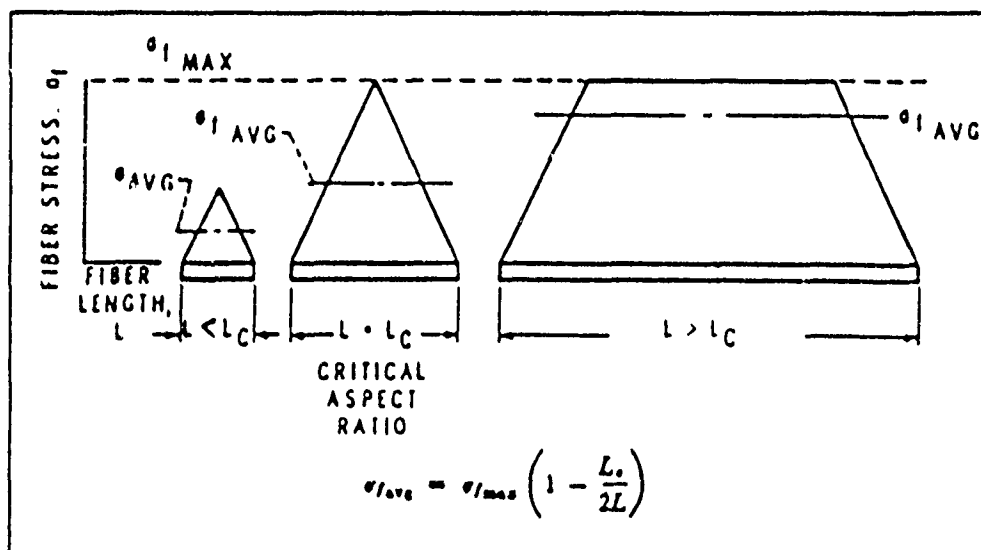
Figure 3. Fiber stress distribution. Tensile stress gradient on fiber versus length (ref 30).

Strength of Ribbon-Reinforced Composites:

When stressed parallel to the axis, the tensile stress of ribbon-reinforced composites may be expressed by the usual rule of mixtures formula, Eq. (6). In the direction perpendicular to the ribbon axis (refs 33,34), the tensile strength is given by

$$\sigma_c = \sigma_m'(1 - V_r) + \sigma_r V_r (1 - \frac{1 - \beta}{W/W_c}) \qquad (11)$$

where V_r is the volume fraction of the ribbon; β is a constant $\cong 0.5$; W is the ribbon width; and W_c is the critical ribbon width necessary for the transfer of

stress to the ribbon from the matrix. The critical width depends on the strength of the ribbon, σ_r, the shear strength of the matrix at the interface, τ, and the ribbon thickness, t:

$$W_c/t = \sigma_r/\tau \qquad (12)$$

It is possible, by employing wider ribbons, to obtain transverse strengths close to the longitudinal strength. Also, it has been demonstrated (ref 35) both theoretically and experimentally (ref 36) that the elastic modulus in the transverse direction approximates the longitudinal modulus.

Flakes: (ref 37)

Flake-reinforced composites that have been examined for structural applications are perhaps the least known. There are many applications where the two-dimensional elements of flakes are preferable to the one-dimensional nature of fibers.

Flakes can be highly packed with their planar reinforcement being their major advantage. Metal flakes can be used as electrical or thermal conductors and nonconductive flakes can serve as insulators. The most widely used flakes for the latter application are glass and mica. Some of the other candidate flakes are aluminum diboride, beryllium, and graphite. The rule of mixtures can also be applied to flake-reinforced composites.

Bond Strength Requirements:

In order to transfer the stress from the matrix to the filament, a specified bond strength, which is measured in shear, must be exceeded. If it is assumed that the filaments are perfectly round with a radius, r, and length, ℓ, encapsulated in the matrix, the following equation must be satisfied for optimum stress transfer (ref 38):

$$\pi r^2 \sigma_f = 2\pi r \ell S_b \quad \text{or} \quad S_b = \frac{\sigma_f}{2\ell/r} \qquad (13)$$

where S_b is the minimum bond strength required and σ_f is the filament strength.

13

For small values of ℓ (which may be the case with discontinuous fiber composites or composites with many interfacial voids), S_b may be quite large. Thus, it becomes exceedingly important that the conditions for maximum adhesion be established.

REQUIREMENTS FOR HIGH PERFORMANCE COMPOSITES

Some of the problems which have to be addressed in the production of high performance composites are interfacial reactions, bond strength, and voids. The requirements essential to a satisfactory particle-type composite are usually also applicable to fiber-reinforced composites. Important requirements for a successful reinforced composite are

- The tensile strength and modulus of elasticity of the reinforcement should be higher than those of the matrix metal.
- The bonding of the reinforcement and matrix interface should be sufficient for efficient transfer of shear stress from matrix to reinforcement during loading in a direction parallel to the reinforcement.
- The reinforcement and matrix should be thermally compatible and free of chemical interaction.
- For maximum strength in a given direction, the composite should have a minimum of voids with the reinforcement aligned parallel to the tension axis and uniformly spaced and separated in the matrix.

ELECTROCOMPOSITES

Theory of Particle or Fiber Encapsulation

Two methods that are commonly known for the encapsulation of particles are conventional electrocodeposition (CECD) and sediment codeposition (SCD). While some of the early investigators proposed or suggested a possible mechanism of

particle capture during deposition, little attention was given to the theoretical details. The three proposed mechanisms which have generally been reported in the literature are: mechanical entrapment, electrophoresis, and the adsorption of particles on the cathode surface. The possibility of electrophoretic forces playing a role in capturing the particles was suggested by Withers (ref 39) and Baimakov and Zhurin (ref 40) in the early 1960's. Martin and Williams (ref 41) reported particle capture by entrapment during rapid plating. Brandes and Goldthorpe (ref 42) noted adsorption forces of ions on the particle surface. Tomaszewski and co-workers (ref 43) investigated the effect of monovalent cations and aliphatic amines in influencing codeposition of inorganic particles from an acid copper bath and found that cationic additions such as thallium enhanced particle codeposition. Chen et al. (ref 44) found that additives do not promote the codeposition of gamma-alumina from the acid copper bath, but oxides of the stable crystalline form, such as alpha-alumina and rutile titania, are favorably codeposited. Foster and Kariapper (ref 45) investigated the streaming potential and adsorption of nickel and copper ions on aluminum and the improvements with additions of thallium and rubidium ions.

As experimental studies continued on particle codeposition, increasing attention was given to the theory of particle encapsulation. Saifullin and Khalilova (ref 46) presented a formula to calculate the particle concentration in electrocomposites. Bazzard and Boden (ref 47) proposed a mathematical expression for the codeposition of solid conducting particles with metals, but did not consider the effects of pH, temperature, or bath constituents.

In 1972, Guglielmi (ref 48) received considerable attention on his investigation of the kinetics of codeposition of inert particles from an electrolyte in which he considered the combined effect of adsorption and electrophoretic forces. He presented a mathematical model to describe the

process based on the interesting similarity of the curves relating v/o of code-

posited particles versus suspended particles with the well-known adsorption

isotherm. Figure 4 is a revised schematic of Guglielmi's model to better

describe his proposed mechanism which involves two adsorption steps:
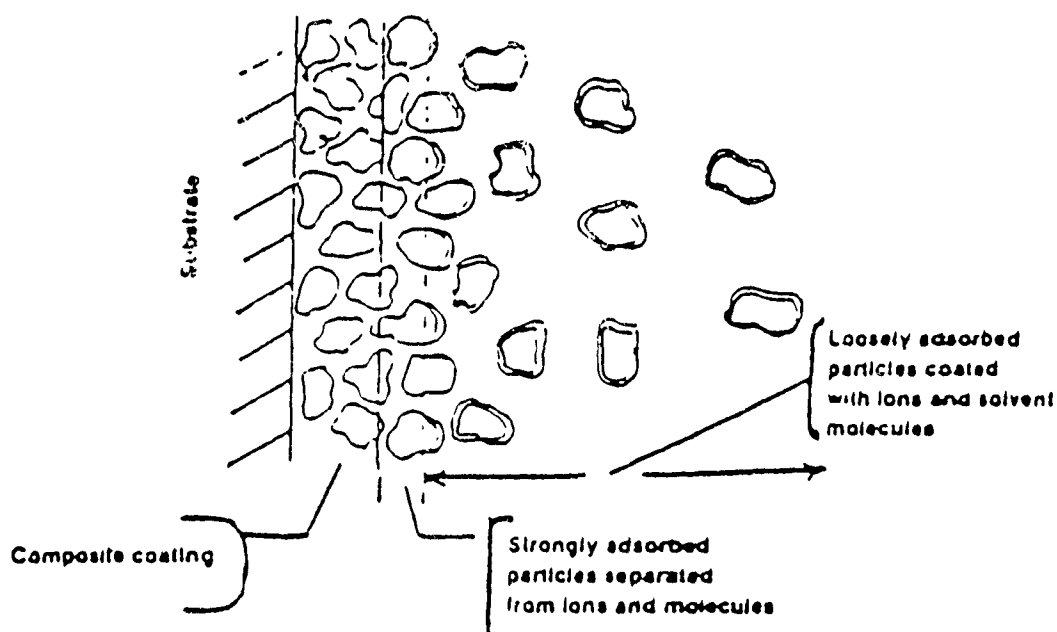
Figure 4. Revised schematic of the two-step deposition process
of the Guglielmi model.

1. The loosely adsorbed particles in the outer layer are coated with a

thin layer of ions and solvent molecules that may screen any interaction

between the particles and the electrons.

2. The second step involves the more rigidly adsorbed particles in the

inner layer. The electrical field existing at the interface helps to uncover

the particles so that a stronger field-assisted adsorption takes place.

A quantitative treatment of the proposed model was presented and subjected

to experimental verification. The adsorption of particles in the outer and

inner layer described above is analogous to the adsorption of ions in the

Hemholtz electric double layer. For the proposed model, the following equation

was devised relating volume fraction of embedded particles (α) to the suspension

concentration of particles (C) and the electrode overpotential (η):

$$\frac{\alpha}{1 - \alpha} = \frac{nFdv_0}{Wi_0} \cdot e^{(B-a)} \cdot \frac{kC}{1 + kC} \tag{14}$$

where: F = Faraday constant

n = balance of electrodeposited metal

W = atomic weight of electrodeposited metal

i_0 = exchange current density

d = density of the metal

i_0 and A are related to metal deposition and are constants in the Tafel equation, which gives a relation between current density (i) and overpotential (η):

$$i = i_0 \cdot e^{A\eta} \tag{15}$$

v_0 and B are related to particle deposition and play a symmetrical role with i_0 and A. K is derived from the Langmuir adsorption isotherm and depends on the intensity of interaction between particles and cathodes.

In the restricted case of low values of α, the factor $(1-\alpha)$ can be dropped and Eq. (14) can be rearranged as follows:

$$\frac{C}{\alpha} = \frac{Wi_0}{nFdv_0} \cdot e^{(B-A)\eta} \cdot (\frac{1}{k} + C) \tag{16}$$

Since Guglielmi proposed his mechanism for particle encapsulation, a number of investigators have demonstrated its validity with alpha- and gamma-alumina in copper using the sulphate bath (ref 49); chromium-graphite system (ref 50); nickel-tungsten carbide (ref 51); gold-silicon carbide and gold-tungsten carbide (ref 52); and more recently with the nickel·tin-silicon carbide system (ref 53). However, the model did not hold for zinc-phenol resin particles in rigorously agitated electrolytes (refs 54,55) or the chromium-alumina system (ref 56).

Dunkerly et al. (ref 57) found that when the concentration of electrolyte exceeded a critical value, the magnitude of the zeta potential decreased drastically and the particles no longer had sufficient charge to repel each other. They also stated that the electrophoretic repulsive forces involved are too small when the suspended particle concentration is large and these are obscured by the higher forces of mechanical stirring and ultrasonic vibration that are employed. In 1966 Hoffman and Mantell (ref 58) observed no electrophoretic effects in the codeposition of alumina in copper in the sulfate bath which is in contrast to other studies (ref 49). Adsorption of organic additives on silica produced a positive surface charge changing the zeta potential in the formation of the gold-nickel-silica composites (ref 59). Foster and Kariapper in their studies (ref 60) indicated that particle encapsulation is strongly influenced by a surface charge produced by the strong adsorption of metal ions onto the particle surface with nickel-alumina and copper-alumina. Particle encapsulation in a copper cyanide bath was much greater than the acid baths. Brandes and Goldthorpe (ref 42) made similar observations.

Based on the number of investigators who found Guglielmi's model to be valid when applied to their own experiments, some degree of merit should be given to his mathematical treatment. However, refinement seems justified since the model does not provide for important process parameters such as effect of size, type, and pretreatment of particles (ref 44,49), effect of bath constituents (ref 61), bath pH (ref 62), temperature, and hydrodynamic effects (ref 63).

Foster and Kariapper (ref 45) proposed a formula which appears to answer the hydrodynamic effects, but the complex interrelationship between some of the associated factors indicates that quantitative treatment of proving its validity may be limited.

In a more recent study, Celis et al. (ref 64) acknowledged the worthy contributions of Foster and Kariapper (ref 45) and Guglielmi (ref 48) in providing a better understanding of the mechanism of particle deposition. At the same time, however, they critically reviewed the inadequateness of their quantitative treatment and the uncertainties reported in the literature and proposed a more extensive mathematical model.

Up to this date, the latter model appears to be the most comprehensive treatment for attempting to elucidate the mechanism of inert particle codeposition. However, it will undoubtedly also be regarded as too complex for quantitative treatment because of a number of limitations.

In determining the validity of the model (ref 64), steady-state conditions must exist and the following should be assured:

- A constant voltage, temperature, pressure, and concentration should be maintained during the process.

- The particles should be uniformly suspended in solution.

- The exposure of the cathode surface to the plating solution should be uniform.

- Both the free and adsorbed ionic species are considered equal with respect to transport and reduction processes.

Evaluation of Mechanism of Particle Encapsulation

From the experimental results reviewed, one may conclude that electrophoresis may or may not play a role in the mechanism of encapsulation of particles or fine fibers in an electrodeposited metal matrix. It should be evident from these results that electrophoretic forces depend on the particular bath suspension and plating conditions employed and the idea of a combined effect taking place may seem very plausible.

In an attempt to form a reasonable concept of the mechanism of particle codeposition, one must also consider the following:

- Plating baths normally include high concentrations of electrolytes in which electrokinetic phenomena would be expected to disappear because the double layer is compressed about the particle and also because the increase in electrical conductivity would cause the electrokinetic action to diminish.

- The particle size and shape are also important parameters.

- The actual current density changes with the adsorption and encapsulation of particles on the cathode surface in which the particles may be conductive or nonconductive.

Preparation, Plating Conditions, and Properties of Electrocomposites

Dispersion-Hardened and Particle-Reinforced Composites:

The optimum conditions for preparing particle suspensions and codepositing a designated v/o of uniformly dispersed inert particles in a metal matrix have not been completely established. Most of the data in the literature have been empirical in nature in which various type particles and electrolytes were employed with a wide variety of conditions. Some of the extreme limits found in the literature are as follows:

- Particle diameter: ranged from 0.02 μm (ref 62) to 100 μm (ref 65)

- Particles in bath: ranged from 5 g/ℓ (ref 63) to 200 g/ℓ (refs 17,57) and in one study for chromium carbide, they exceeded 500 g/ℓ (ref 66)

- Particles in deposit: up to 57 v/o for nickel-tungsten carbide (ref 51) and exceeding 60 v/o for nickel-molydisulfide (ref 67)

- Current density: exceeded 30 A/dm^2 for nickel-molydisulfide (ref 67)

Some of the practices and observations reported in the preparation of code-posited particles are:

20

Preparation of Suspension - The cleaning of particles prior to immersion in the electrolyte may have a significant effect on the final size and amount of encapsulation in the matrix metal depending on the grade and purity of the particle.

The acid cleaning of corundum white and gray powders (alumina) resulted in large particle-size reductions and differences in rates of particle capture in nickel (ref 65). In other studies, boiling copper sulfate electrolyte was used to preclean alumina, silicon carbide, and barium sulfate particles (ref 68) and tungsten carbide particles were immersed in acetone and diluted hydrochloric acid in order to activate the contaminated particle surface for encapsulation in nickel (refs 51,63).

Two methods which were successfully employed to prepare solution-particle suspensions (refs 17,62) are

- Immersing the particles directly into the electrolyte and mixing with a magnetic stirrer or preferably with a blender.

- Suspending the particles in a small portion of water and mixing with a blender; conventional electrolyte concentrate can then be added to the blended slurry and prepared for plating; the blending time can be determined experimentally.

Factors Affecting Particle Encapsulation -

- Particle Concentration - Increased particle concentration in the bath is the most effective variable for increasing the v/o of dispersoids in the matrix (refs 17,47,56,60,62) which approached a maximum in some studies (refs 63,69).

- Additives - Wetting agents or monovalent cations and aliphatic amines produced a surface change when adsorbed on a particle (refs 17,43,58,70) promoting particle encapsulation and improved dispersion. In other studies,

organics caused foaming and particle floatation (ref 60) and adverse dispersing (ref 42), while other investigators found no effects (ref 44).

- Current Density - The concentration of particles (alumina, silicon carbide, chromium carbide, and molydisulfide) in the deposit generally decreased as the current density increased (refs 17,53,62,67), however, no effects were observed with graphite in chromium (ref 50). In one study (ref 71), particles were only encapsulated in chromium at low current density (2-4 A/dm^2).

- Type of Bath - Particle encapsulation is less in a copper sulfate bath than a cyanide bath (refs 42,43,58). The presence of chloride ions inhibited the codeposition of oxides with copper (ref 72) in the sulfate bath. Particle encapsulation in an electroless bath was also investigated (ref 73).

- Type of Particle - The encapsulation of rutile titania (0.3 μm) is greater than alpha-alumina (0.05 μm) in nickel (ref 17); alpha-alumina (0.3-1.0 μm) and rutile titania (0.3 μm) are readily codeposited in copper (acid bath), while gamma-alumina (0.2 μm) and anatase titania are not (ref 44). Calcining promoted codeposition of alpha-alumina particles in copper (ref 44).

- Current Mode - The use of pulse or periodic reverse currents has resulted in copper-alumina composites where concentrations of particles increased with increasing current density (refs 74,75) which is in contrast to normal direct current plating reported above. Microstructural changes of the matrix metal, improved particle dispersion, and composite strength retention at high temperatures have also been observed when pulse or periodic currents are employed (refs 74,76,77).

- Ultrasonics - Ultrasonic agitation was found to reduce agglomeration and improve particle distribution and strength retention of copper-alumina (ref 76) and nickel-alumina (ref 75).

• Bath Temperature - The influence of temperature on the codeposition of particles is not very well defined. Codeposition decreased with increasing temperatures up to 50°C for graphite powder in chromium (ref 50) and concentrations of silicon carbide and alumina in tin·nickel and nickel, were found to be independent of temperature (refs 53,62).

• Bath pH - The influence of pH on particle concentration is also not very well defined. No effects were found by increasing pH with the nickel-alumina system (refs 42,43,58), while one investigator noted an increase in particle codeposition with pH up to 2.0 which remained constant above 2.0 (ref 62). Graphite powder increased in nickel with increasing pH, while molydisulfide powder in nickel decreased (ref 78).

Other Particle Dispersions -

Solid lubricants - The production of electrocomposites has included particulates with lubricating properties, such as molydisulfide, tungsten disulfide, and graphite particles (refs 67,78,79,80). High wear resistant properties have been reported with such composites.

Metal particles - Studies have also included the encapsulation of dispersed metal powders in a matrix for the purpose of achieving alloys by post-heating (refs 47,81,82). The benefits derived from this practice are the formation of alloys into complex shapes at considerably lower temperatures and costs than are required for casting.

Electroless composites - Particle-reinforced composites have been produced by electroless plating of nickel (refs 43,83). Particulate matter such as alumina, diamond, silicon carbide, and teflon have been encapsulated in an electroless nickel matrix.

Properties of Particle-Dispersed Electrocomposites - The increase in

as-plated hardness of submicron particle-dispersed composites is significant,

but the strength is marginal (refs 19,84-86). When subjected to high temperatures, their strength retention is fairly significant, however, in order to achieve maximum suspension strengthening, composites must be subjected to a combination of mechanical and thermal treatments. For example, TD-nickel (a well-known high strength alloy) is hot extruded, stress-relieved, and subjected to a prolonged series of moderate rolling reductions and intermediate anneals. The effects of cold rolling copper-alumina electrocomposites have been reported (ref 77) to produce significant strengthening, but embrittlement occurred.

The following discussion of results refers to as-plated and post-heat treated composites without any subsequent mechanical working. A suitable combination of mechanical and thermal treatments to achieve the maximum properties in an electrocomposite containing submicron-sized particles for the purpose of dispersion-strengthening may have to be devised for each system.

In contrast to the dispersion-strengthening, the strengths of particle-reinforced composites may well be at their maximum level in the as-plated condition or may require a post-heat treatment for optimum performance.

Some of the studies reviewed have shown that codeposition of hard inert particles in a metal:

- increases the hardness and strength, but decreases the ductility of various composite systems;

- increases the creep strength of dispersion-hardened gold-alumina (refs 87,88);

- increases the electrical resistivity of dispersion-hardened copper-alumina slightly (ref 77), but aluminum-alumina is not changed (ref 88);

- increases the corrosion resistance of nickel-alumina (ref 89); and

- increases the wear resistance of cobalt-chromium carbide (ref 66), nickel-silicon carbide (ref 90), cobalt-chromic oxide (ref 91), and nickel-diamond (refs 63,92). Increased wear resistance is also obtained with the chromium-silicon carbide and systems using submicron-sized particles (ref 93).

Figure 5 shows the yield strengths versus post-heating for nickel, nickel-alumina, and nickel-titania alloys and also shows cross sections of the microstructure of two of the alloys in the insets (ref 17). Note that these alloys have not been mechanically worked, therefore the plot does not represent their full potential of strength retentions.
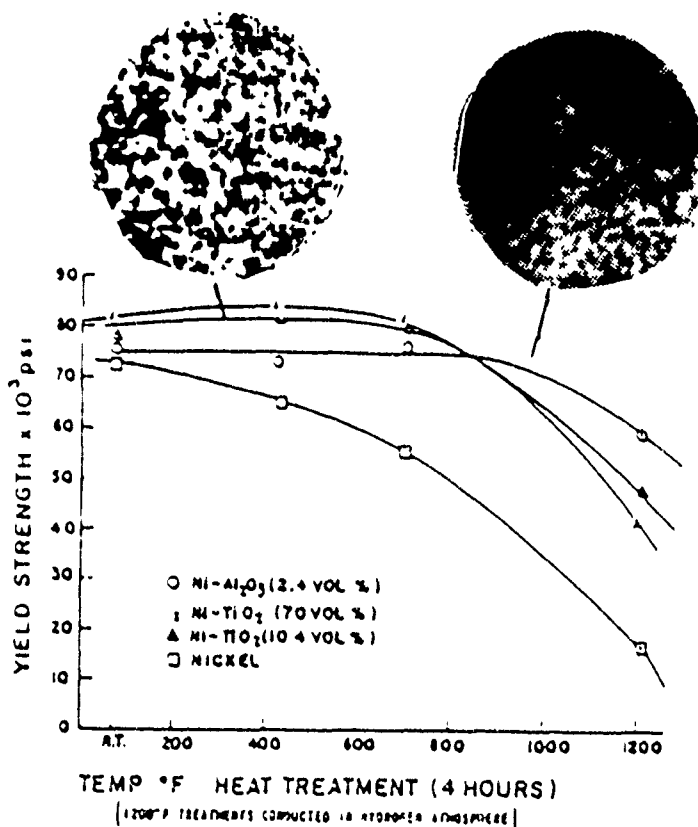

Figure 5. Yield strength versus heat treatment for nickel, nickel-alumina, and nickel-titania (insets are cross sections of the alloys (1000X)).

25

Discontinuous Fiber (Whiskers or Filaments)-Reinforced Electrocomposites:

Preparation of Suspensions - Since whiskers and most high strength

fibers are fragile and easily damaged during handling, great care must be exer-

cised in preparing solution-fiber suspensions. Suggested methods of preparing

suspensions include:

• Immersing the fibers or whiskers directly into the electrolyte and

stirring gently (by air, magnetically, or ultrasonically) during plating.

• Adding the fibers or whiskers gradually into the electrolyte during

plating and relying on gradual settlement of the dispersoids onto a horizontal

cathode surface.

Factors Affecting Encapsulation - The formation of electrocomposites

with discontinuous fibers is by far the most difficult to produce. The dif-

ficulty of encapsulating freely suspended discontinuous fibers increases with

increasing length and diameter of the fiber due to the probable clustering and

pileup on a cathode surface before the fibers are completely encapsulated. The

problem is more complex if the fibers are electrically conductive or if their

surfaces are difficult to wet. However, the optimum plating conditions should

be the same as for particles.

Since whiskers are the most potentially high strength candidate materials

for fiber reinforcement, techniques for their successful encapsulation should be

regarded as a valuable asset.

Properties of Discontinuous Fiber-Reinforced Electrocomposites -

Nickel composites up to 11 v/o alpha-alumina whiskers (30 μm diameter) have been

successfully electroformed in contrast to composites with silicon carbide

whiskers (10 μm diameter) which resulted in excessive voids in the nickel matrix

due to the semiconductive surfaces of the fibers (ref 94). The strengths of the

nickel-alumina alloys (Figure 6), after annealing in H_2 at 650°C for one-half

hour. agree with the calculated rule of mixtures. A cross-sectional view of one of the alloys with 11 v/o alumina is shown in the inset.
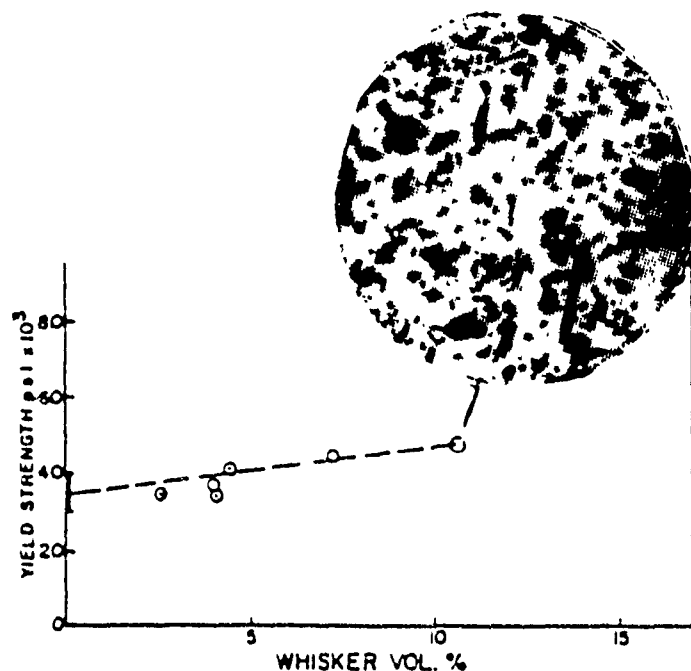

Figure 6. Variations of yield strengths of alpha-alumina whiskers - nickel composites annealed. (Inset is a cross section of the composite).

Continuous Fiber-Reinforced Electrocomposites:

An excellent handbook on the preparation, structure, and properties of reinforcing fibers is by Watt and Perov (ref 95). Continuous filament reinforced composites are potentially among the highest strength and highest performance structural materials that can be produced by electrodeposition. With cylindrical-shaped cathodes, reinforcements can easily be wound on a rotating cathode and encapsulated in a plated matrix metal with complete control of the spacing and v/o of the filament.

The preparation of such composites will depend on the filament characteristics and cathode geometry. Factors that must be considered are

- monofilament or strand

- filament geometry and size

- conductive or nonconductive filament

27

- filament reaction at high temperatures

- pretreatment - cleaning, activating, or etching requirements

- cathode design - cylindrical, oval, etc.

- winding apparatus - spacing, guides, tension, filament breaks, etc.

- winding pattern - unidirectional or cross-wrap

- prewinding or simultaneous winding

Properties and Microstructures of Some Electrocomposites with

Continuous Unidirectional Filaments - A variety of continuous unidirectional filament-reinforced electrocomposites has been produced (refs 18,94,96-105). Some of the systems follow:

- Monofilaments:

  Tungsten (1 mil) in copper

  Tungsten (½ mil) in nickel

  Boron (4 mils) in nickel, copper, or aluminum

  Boron (2 mils) in nickel

  Silicon carbide (4 mils) in nickel

  Boron nitrided coated boron (4 mils) in nickel

- Strand:

  Glass in nickel

  Graphite in nickel or aluminum

Tungsten · Strength measurements of continuous filament-reinforced electro-composites with minimal voids compare favorably with calculated values from the rule of mixtures. The stress-strain plots in Figure 7 show increasing strength with increasing v/o values of 12 μm (½ mil) diameter tungsten filaments in electrodeposited nickel (ref 94). The inset shows a cross section of one of the composites in which the tungsten filament was simultaneously wound on a cathode drum during plating.

28
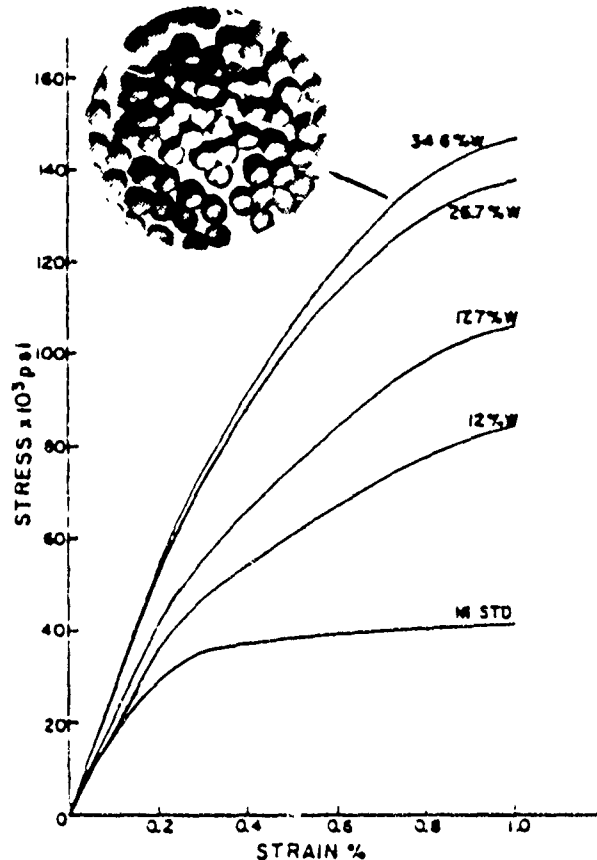
Figure 7. Stress-strain 0.005-inch tungsten filament
in nickel composites (annealed).

Boron and Silicon Carbide - Candidate low density conductive monofilaments

such as boron and silicon carbide are usually supplied in minimum diameters of

100 μm (4 mils) and are not easily encapsulated without voids due to radial

crystal growth of the plated metal around the filament. In this case, the fila-

ment had to be prewound on the cathode drum prior to nickel plating. View "a"

of Figure 8 shows the profiles of plated nickel encapsulating a single conduc-

tive boron filament which has a tungsten core. View "b" shows the voids formed

between two filaments when they are spaced too close (ref 97) during plating.

View "c" shows the increasing interfacial reaction which occurs with temperature

between boron and nickel (ref 18). Fortunately, voids are easily eliminated

when the surfaces of boron filaments are nitrided, making them nonconductive

29

which prevents the radial crystal growth around the filament (Figure 9) and per-
mits higher filament loading (i.e., spacing as close as one-half filament
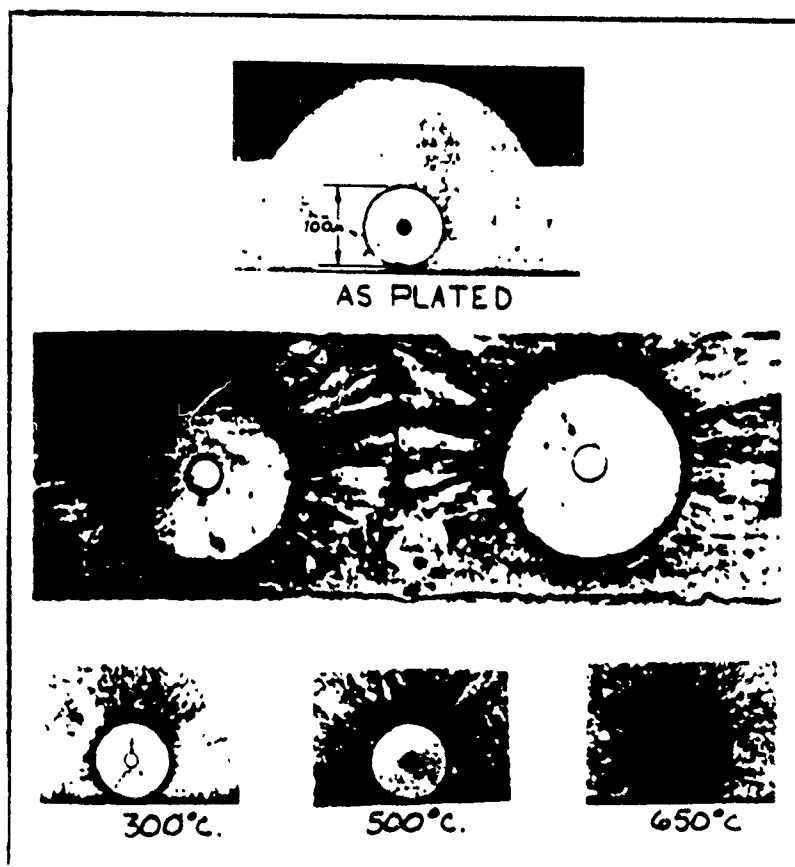diameter).

Figure 8. Nickel-boron (4 mils) composites: (a) nickel contour
over filament; (b) voids formed between filaments;
(c) interfacial reactions with temperature.
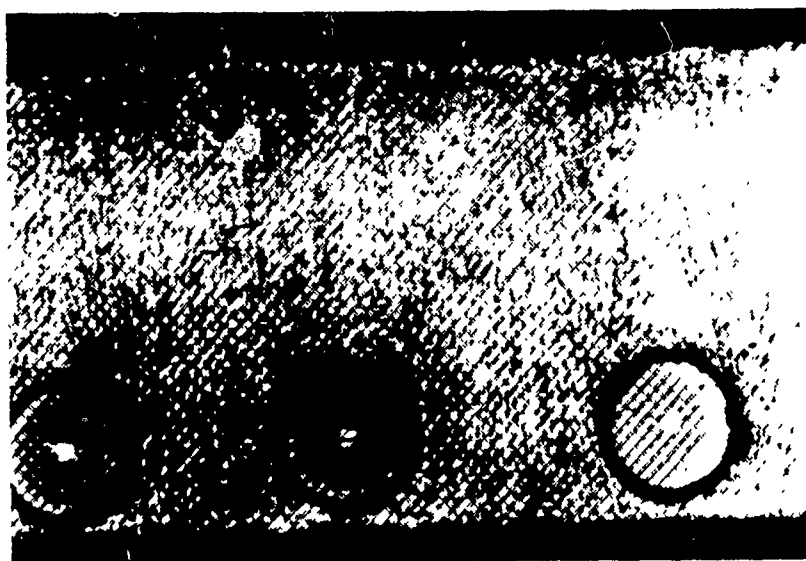
Figure 9.   Cross section of nickel-boron (BN-coated) composite with
            the absence of radial crystal growth of nickel around the
            filaments and subsequently void-free.

Furthermore, the nitrided coating prevents interfacial reactions with

nickel at 650°C as compared with pure boron (Figure 8). Work by Camahort (ref

106) has shown that surface nitridation protects boron from reacting with alumi-

num for ten minutes at 800°C (1470°F).

Equation (13) dictates that as the diameter of the filament increases, the

bore strength requirements increase. Therefore, the bond strength of 100 μm

diameter filaments of boron and silicon carbide in nickel were investigated (ref

18). Results of filament pull-out studies indicated that etching the filament

and post-heating electrocomposites up to 500°C improved the bond strength.

Glass and Graphite - High strength-low density filaments such as glass and

graphite do have small diameters (8-12 μm) which are ideal for encapsulation by

plating. However, such reinforcements are normally supplied in strands con-

sisting of several filaments which are coated with an organic film for use with

an epoxy matrix. For complete encapsulation of the individual filaments in a

metal matrix, the strands have to be thoroughly washed to remove the organic

31

film and carefully spread apart and placed on a cathodic surface prior to plating. Figure 10 shows a cross section of glass fibers in a plated nickel matrix.

Figure 10. Glass filament-nickel composite by
prewound filament technique (200X).

Undoubtedly, graphite has the most potential of all the reinforcements due to its high strength-to-density ratio and thermal stability, but it has poor oxidation resistance. For over the past decade, extensive studies have concentrated on applying various plating coatings on graphite filaments for resistance against reactions with matrix metals such as aluminum.

Table II shows some of the results of different electrocomposite systems reported in the literature.

Composite System		v/o Fil	kg/mm²	10³psi	kg/mm²	10³psi	kg/mm²	10³psi
4 mils B/Ni98 *		42	285	405	42	61	132	188
		51	273	388	63	90	132	188
4 mils B/Al104 *		15	210	300	10	14.3	25.4	32.6
4 mils B/Al105 *		32	-	-	18	25.4	85	121
2-4 mils W/Ni105 *		50	352	500	70	100	155	221
½ mil * W/Ni94 *	as-plated	34.3	352	500	73	104	149	212
	650°C ½ hour	34.6	-	-	39	55	117	166

*Reference numbers.

SUMMARY OF ELECTROCOMPOSITES

Electrodeposition is a viable process for producing sound and high strength composites. However, improvement in the reproducibility of composites and further advancements in plating techniques and filament making are required. From the foregoing, we have learned that successful electrocomposites were produced with the following techniques:

- Conductive filaments with a diameter of 25 μm (1 mil) or less were simultaneously wound on a mandrel during plating.

- Nonconductive filaments of 100 μm (4 mils) diameter were unidirectionally wound in single rows with a minimum spacing of one-half filament diameter followed by plating for complete encapsulation. Then, a second row was wound and plated, etc., without removing the mandrel or interrupting electrolysis when the deposit was relatively smooth.

- Conductive filaments of 100 μm (4 mils) diameter were processed as above with two exceptions: minimum spacing was one filament diameter, and the mandrel was removed after each row was plated to remove surface irregularities by machining.

Two of the changes that will significantly improve the quality of electro-composites are:

- The use of finer diameter (< 50 μm) monofilaments with high strength and high modulus-to-density ratios.
- The use of nonconductive filaments when their diameter is greater than 50 μm (2 mils).

Studies are also needed in:

- Determining the benefits of other pretreatments to improve the wetting and bond strength of filaments.
- Expanded use of ultrasonics, periodic reverse, pulse plating, and other aids to determine their influence on voids and properties of the matrix metal.
- The plating of matrix alloys.

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